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Contaminant Survey of Cache River National Wildlife Refuge including Radcliffe Farms, Arkansas.

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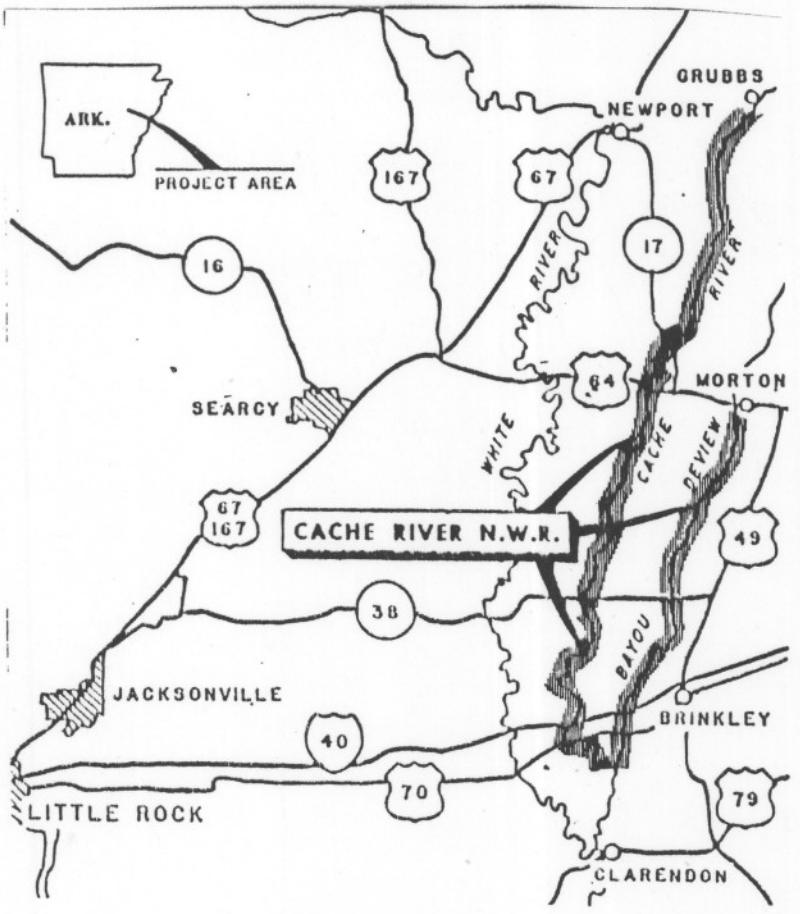

Submitted
by

Stephen B. Smith and Lloyd Inmon
Fish and Wildlife Enhancement Office
Vicksburg, Mississippi
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Introduction

The Fish and Wildlife Service (Service) has identified the bottomland hardwoods of the Lower Mississippi River Delta as one of the highest Service priorities for waterfowl habitat within the United States. The Cache River National Wildlife Refuge (CRR) has been recognized as a high value basin in the Mississippi Delta for wintering migratory waterfowl (Quackenbush et al. 1984). The Cache River Basin was named in 1990 as a "Wetland of International Importance", in the same class as the Everglades and Okefenokee Swamp (White 1990). The CRR, located in northeast Arkansas (Figure 1), is a new refuge which currently has approximately 17,000 acres, about halfway to the goal of 35,000 acres. The Cache River Basin is subject to agricultural runoff from upstream and surrounding farmlands. Even though the use of organochlorine (OC) pesticides has drastically declined, these compounds have a slow rate of decomposition. It is therefore essential to analyze fish samples to determine if agricultural runoff is impacting the resources on the Cache River Refuge. An initial survey was approved for FY 1988; however, because of a drought, it was impossible to collect samples. In May 1989, fish samples were collected on the CRR for OC and metal residue analyses. A crop duster landing strip on the former Radcliffe Farm site, which is now part of the CRR, was observed to be devoid of vegetation. As a result, additional samples of soils adjacent to the landing strip and near a fuel storage tank were collected in early 1991 for OC and aliphatic hydrocarbon residue analyses.

Study Sites

Fish collections for the contaminant survey were made at five sites on and near the CRR (Figure 2), which were accessible by boat and contained representative fish species. The locations of the sites are described in Table 1.

Collections of soils were made at the Radcliffe Farm site on the CRR for residue analysis (longitude 91° 21', latitude 35° 05'). Four of the samples were collected in a small area at the end of an abandoned air strip. Two additional samples were collected near diesel tanks used for fuel storage (Figure 3).

Methods

Fish were collected using a direct current boom electrofishing boat. All fish were measured, weighed, wrapped in aluminum foil, and kept on ice until they could be frozen. Analyses of inorganic compounds (aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, cobolt, chromium, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, thallium, tin, vanadium, zinc) were completed using inductively coupled plasma emission measurement, graphite furnace atomic absorption measurement, and cold vapor atomic absorption (Research Triangle Institute 1990). Organic analyses for organochlorine pesticides [hexachlorobenzene, oxychlordane, heptachlor epoxide, cis & trans chlordane, cis & trans nanochlor, toxaphene, dieldrin,

Figure 1. Location of Cache River National Wildlife Refuge, Arkansas

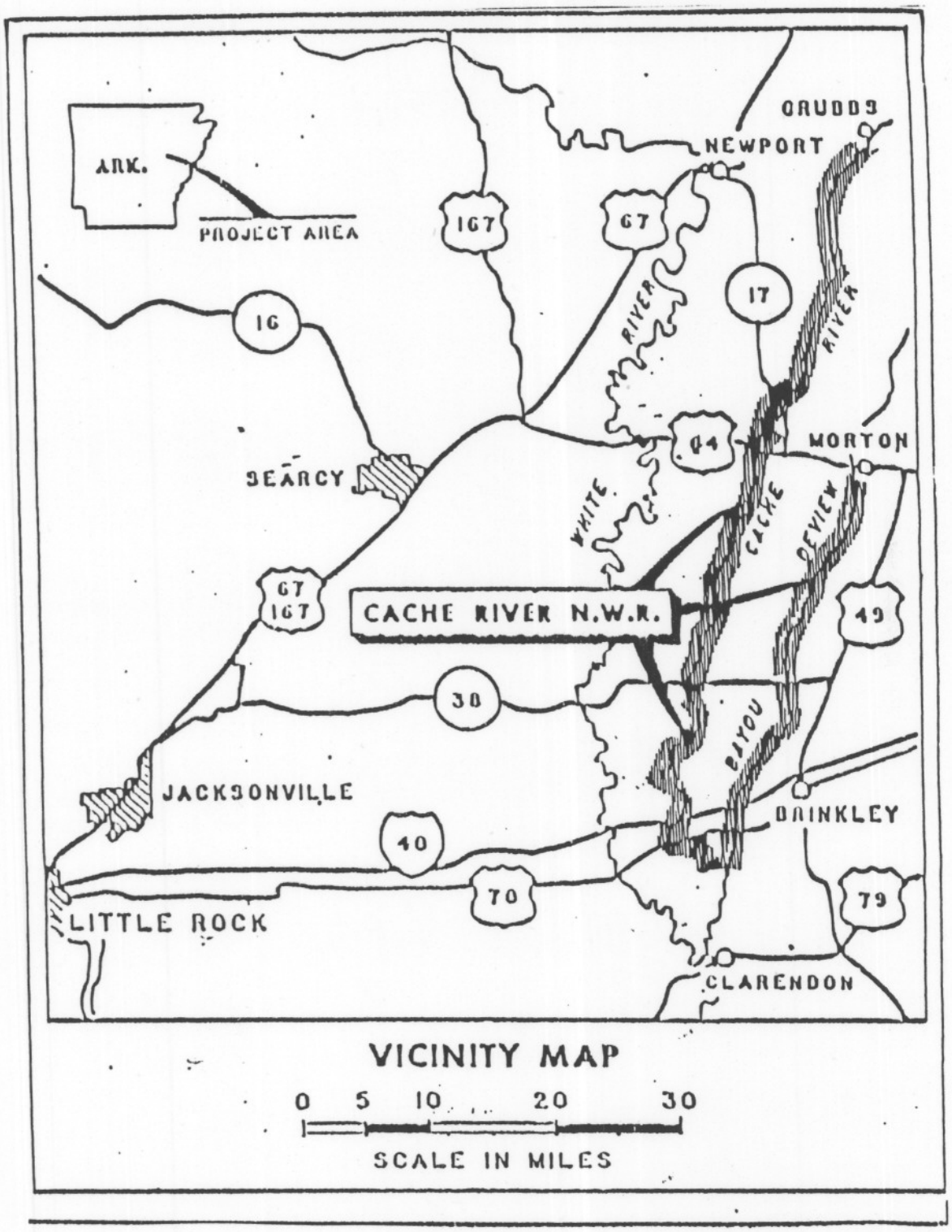

Figure 2. General locations of fish tissue collection sites (May 1989) for the contaminant survey of the Cache River National Wildlife Refuge, Arkansas.

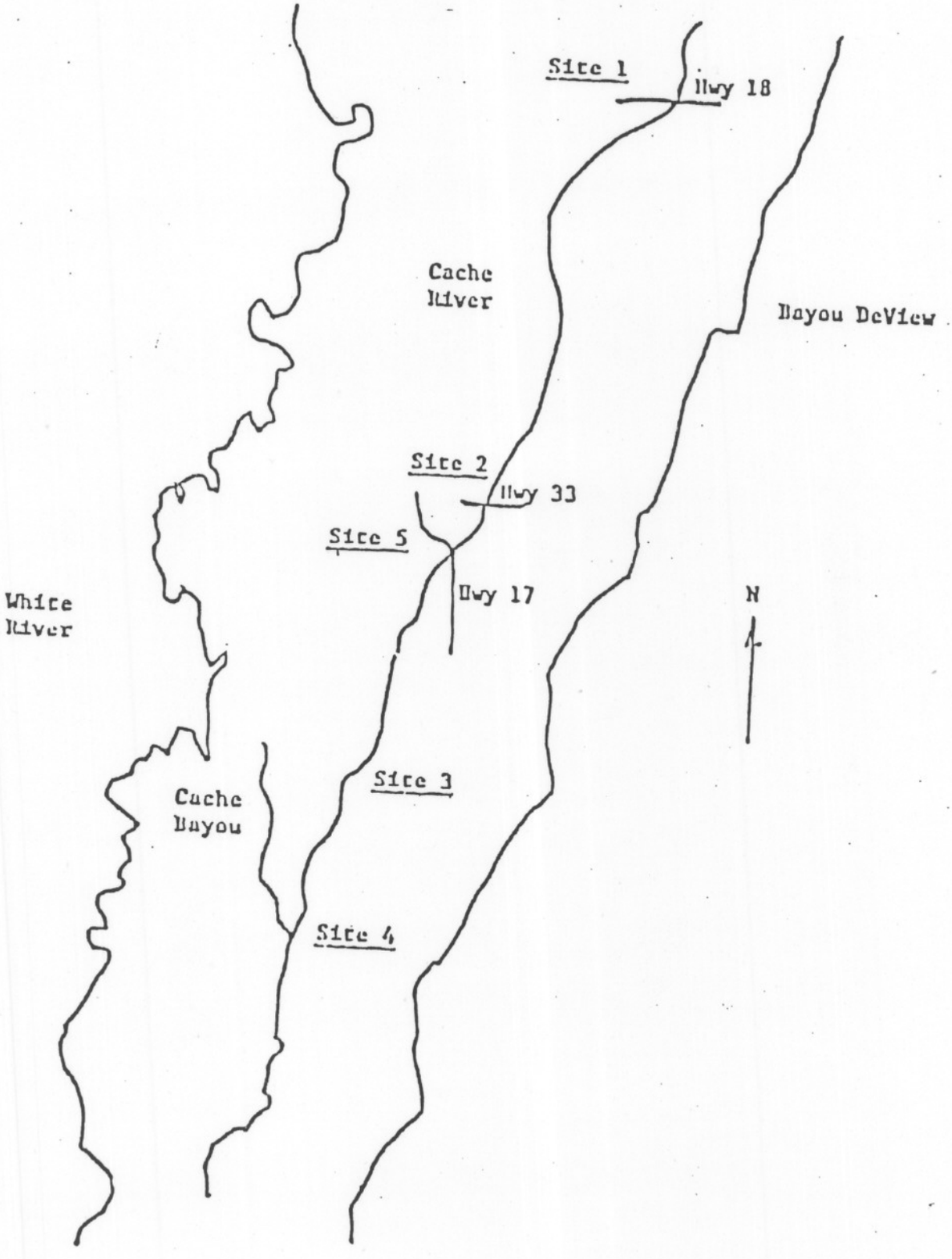

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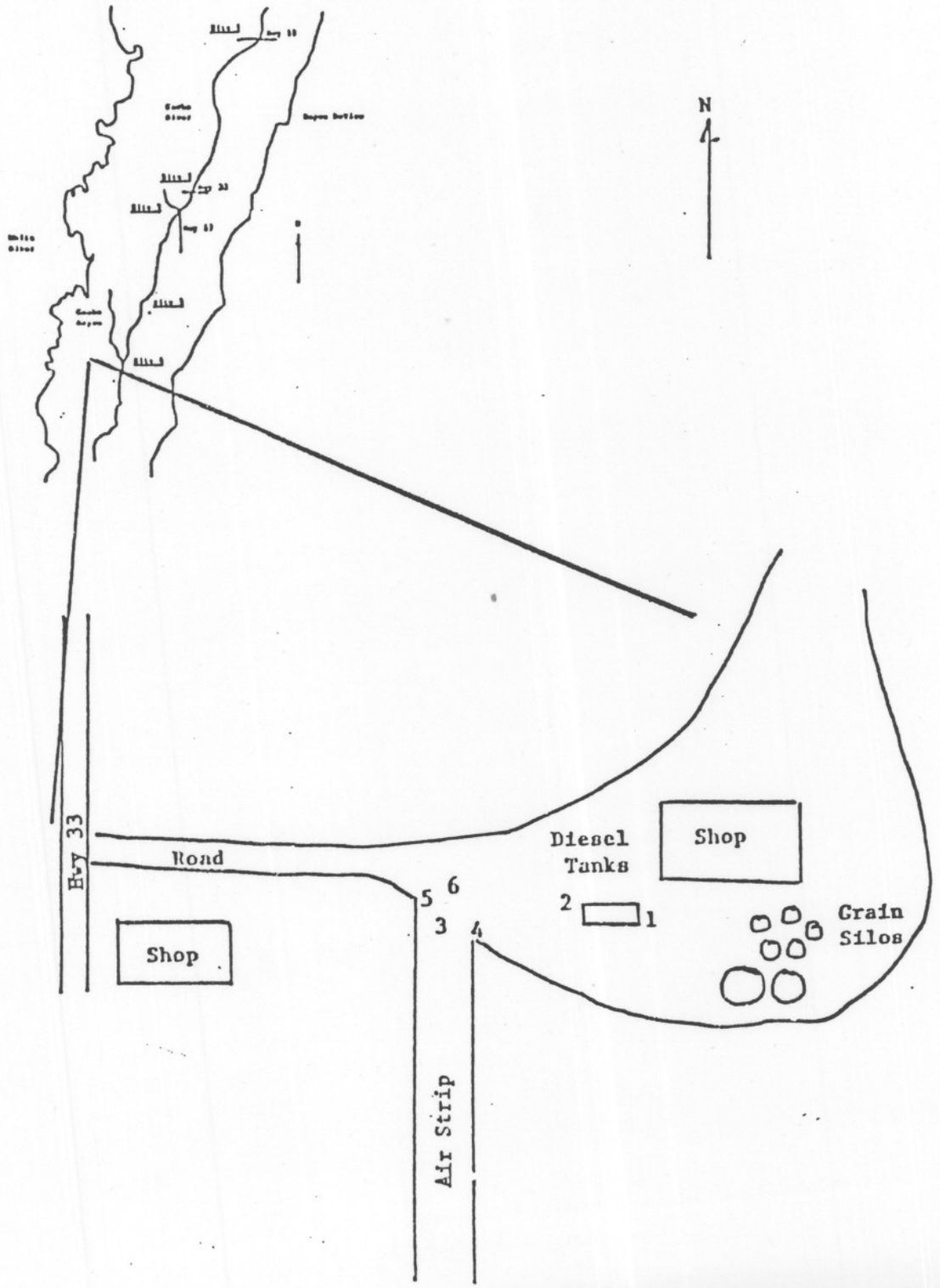
Table 1. Locations of the fish collection sites (May 1989) for the contaminant survey of Cache River National Wildlife Refuge, Arkansas

Site	Location
1	near Highway 18 bridge on Cache River: longitude 91 degrees 3 minutes, latitude 35 degrees 38 minutes
2	Highway 33 bridge on Cache River: longitude 91 degrees 10 minutes, latitude 35 degrees 22 minutes
3	inside Rex Hancock WMA[1] on Cache River: longitude degrees 17 minutes, latitude 35 degrees 91 minutes
4	confluence of Cache Bayou and Cache River: longitude 91 degrees 18 minutes, latitude 35 degrees 4 minutes
5	Highway 17 bridge on Cache River: longitude 91 degrees 12 minutes, latitude 35 degrees 20 minutes

[1]WMA - Wildlife Management Area

Figure 3. Location of soil sample collection sites at Radcliffe Farm on the Chache River National Wildlife Refuge, Arkansas



dichlorodiphenyltrichloroethane (DDT), DDT metabolites (DDD and DDE), endrin, and mirex] and polychlorinated biphenols (PCB) were completed with a ten gram sample which was mixed with anhydrous sodium sulfate and soxhlet and extracted with hexane for seven hours. The extract was concentrated by rotary evaporation, transferred to a tarred test tube, and further concentrated to dryness for lipid determination. The lipid sample was dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Residues were partitioned into petroleum ether and transferred to a glass chromatographic column containing 20 grams of Florisil. The column was eluted with 200 ml 6% diethyl ether/94% petroleum ether (Fraction I) followed by 200 ml 15% diethyl ether/85% petroleum ether (Fraction II). Fraction II was concentrated to appropriate volume for quantification of residues by packed capillary column electron gas chromatography. Fraction II contained the compounds dieldrin, endrin, dachal, and PCBs. The remainder of the organochlorine compounds was contained in Fraction I (State Chemical Laboratory 1990).

Soil samples were collected using a sterile spatula to dig through the upper surface layer. Composite samples were placed in a pre-cleaned glass jar and kept on ice until they could be frozen. A 25 gram soil sample was extracted with acetone, followed by petroleum ether, by allowing it to soak one hour in each with intermittent shaking. A final acetone/petroleum ether extraction was done, and the extract combined, centrifuged, and transferred to a separatory funnel containing sufficient ether to facilitate partitioning of residues into a petroleum ether portion. The petroleum ether was washed twice with water and concentrated by Kuderna-Danish to appropriate volume for transfer to a 20 gram 1% deactivated silica gel column, topped with five grams neutral alumina. Aliphatic hydrocarbon residues were fractionated by eluting aliphatics from the column with 100 ml petroleum ether (Fraction I) using first, 100 ml 40% methylene chloride/60% petroleum ether, then 50 ml methylene chloride (combined eluates, Fraction II). If needed, Faction I containing aliphatics was subjected to additional cleanup by concentration and transferred to a deactivated (2% water) Florisil column. Aliphatic residues were eluted from the Florisil column using 200 ml 6% diethyl ether/94% petroleum ether. The eluate was concentrated to appropriate volume for quantification by capillary column, flame ionization gas chromatography (State Chemical Laboratory 1991).

Comparisons of concentrations of inorganic and organic compounds in the fish tissue from on and near the CRR were made to the concentrations found in fish collected from the White River near DeValls Bluff Arkansas for the National Contaminant Biomonitoring Program (NCBP) fish collections (Schmitt and Brumbaugh 1990). Comparisons of the fish tissue data were also made to the 85 percentile level of the mean values determined from all samples collected within the United States. Levels above the 85 percentile were considered to be elevated (Schmitt and Brumbaugh 1990). Data from sediments collected at the Radcliffe Farm site were compared to values from Bolton et al. (1985) and Long and Morgan (1990) to determine elevated levels of soil contaminants.

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Results

Concentrations of inorganic compounds detected in fish tissue from the five sampling sites are presented in Appendix A, Tables A1-A5. The summary of mean concentrations of priority pollutant inorganic compounds (U.S. Environmental Protection Agency 1986) in fish tissue from these sampling sites is found in Table 2. Each fish sampling site exceeded the 85 percentile for copper and mercury. Samples collected from the Rex Hancock Wildlife Management Area (Site 3) and at Highway 17 (Site 5) had concentrations of zinc in the fish tissue that exceeded the 85 percentile. The same sites (Sites 3 and 5) also exceeded the values for copper, mercury, and zinc that were found in fish tissue taken from near Devalls Bluff, Arkansas in the White River during the National Contaminant Biomonitoring Program (NCBP) (Table 2). Chromium was not determined in fish samples from the NCBP. All concentrations of chromium from the sampling sites were below EPA recommended levels for fish tissue concentrations (53.8 ppm).

Table 3 compares the mean concentrations of inorganic compounds in predator fish (spotted gar and white crappie) with the mean concentrations in benthic feeding fish (smallmouth buffalo and carp). There appear to be significant differences in concentrations of zinc between predator fish and benthic feeders, however, due to small sample size, statistical differences were not indicated. Major differences were not apparent in concentrations of copper and mercury between the predator fish (spotted gar and white crappie) and the benthic feeders (smallmouth buffalo and carp). However, there does appear to be a higher concentration of selenium in the benthic feeders.

Regarding organic compounds in fish tissue; DDT, DDD, DDE, and dieldrin were the only organochlorines detected (trans-Nanochlor was detected at 0.01 ppm in two fish at Site 5 only) in the fish tissue samples from the CRR (Appendix A, Table A6). The mean values for DDE, DDD, DDT, and dieldrin (Table 4) exceeded the 85 percentile at each station except at Highway 18 near Grubbs, Arkansas (Site 1). The highest DDE, DDD, and DDT and dieldrin concentrations were found in smallmouth buffalo (*Ictiobus cyprinellus*) collected from the Cache River at Site 5. DDD and DDE, the metabolites of DDT, were present in all 11 fish samples.

The mean concentrations of organochlorine compounds detected in predator fish and benthic feeders are provided in Table 5. The concentrations of the organochlorine compounds were greater in the benthic feeding fish than in the predator fish, particularly for DDE and DDT. This abnormality of higher concentrations of organochlorines in benthic fish than in predator fish may not reflect the true situation and could be an artifact of the small sample size.

The soil samples from the six sites at Radcliffe Farm (see Figure 3) indicated high levels of organochlorine compounds near the end of the crop duster landing strip (Appendix A, Table A7). Both toxaphene and DDT and its metabolites were detected at very high levels for soil sampling Sites 3, 4, 5, and 6 (Table 6). High concentrations of aliphatic hydrocarbons were found at soil sampling Sites 1 and 2 near the diesel fuel storage tanks (Appendix A; Table A8, and Table 6).

Table 2. Mean concentrations (mg/kg-ppm, wet weight) of priority pollutant inorganic compounds detected in fish samples collected for the contaminant survey of the Cache River National Wildlife Refuge, May 1989. Comparisons to concentrations of compounds from the National Contamiant Biomonitoring Program (NCBP) on the White River at Devalls Bluff, Arkansas and the 85 percentile of national average concentrations. Number of fish in ( ), dry weight in [ ].

	Chromium	Copper	Zinc	Mercury	Selenium
Site 1					
Spotted Gar (1)	1.6 [5]	1.2 [4]	27 [86]	0.30 [1.0]	ND[1]
Smallmouth Buffalo (3)	0.6 [2.3]	1.4 [5.3]	17 [64]	0.26 [0.9]	ND
Site 2					
White Crappie (1)	0.6 [3]	0.9 [4]	19 [78]	0.34 [1.4]	ND
Smallmouth Buffalo (3)	0.7 [2.3]	1.7 [6]	17 [59]	0.30 [1.0]	0.14 [0.7]
Site 3					
Spotted Gar (1)	1.3 [5]	1.5 [5]	18 [65]	0.66 [2.4]	ND
Smallmouth Buffalo (2)	0.8 [2.5]	1.8 [5.5]	221 [744]	0.24 [0.8]	ND
Site 4					
Spotted Gar (1)	1.8 [6]	1.1 [4]	28 [88]	0.46 [1.5]	ND
Smallmouth Buffalo (2)	0.9 [3]	1.9 [6]	18 [60]	0.44 [1.5]	0.18 [0.5]
Site 5					
Spotted Gar (2)	1.7 [6]	4.5 [14]	25 [44]	0.41 [1.5]	0.16 [0.5]
Carp (1)	0.7 [2]	2.6 [9]	83 [287]	0.36 [1.0]	0.16 [2.0]
Smallmouth Buffalo (3)	0.6 [2]	2.5 [8]	16 [54]	0.43 [1.7]	0.55 [1.0]
NCBP, White River, AR	NA[2]	0.57	44	0.21	0.33
National 85%	NA	1.0	40.2	0.18	0.74

1- No data

2- Not available

Table 3. Weighted mean concentrations (ppm-wet weight) of priority pollutant inorganic compounds from fish samples collected on the Cache River National Wildlife Refuge, May 1989. Number of samples in ( ), Range of values in [ ].

	Copper	Zinc	Mercury	Selenium
Spotted Gar (5) *Lepisosteus oculatus*	2.6 [1.1-4.5]	25 [18-28]	0.45 [0.30-0.66]	0.06 [ND-0.16]
White Crappie (1) *Pomoxis annularis*	0.9	19	0.34	ND
Smallmouth Buffalo (13) *Ictiobus bubalus*	1.9 [1.4-2.5]	48 [17-221]	0.33 [0.24-0.44]	0.18 [ND-0.55]
Carp (1) *Cyprinus carpio*	2.6	83	0.36	0.16

ND - Not Detected

Table 4. Mean concentrations (ppm-wet weight) of organochlorine compounds analyzed in fish collections for the contaminant survey of the Cache River National Woldlife Refuge, May 1989. Comparisons to concentrations of compounds from the National Contamiant Biomaonitoring Program (NCBP) on the White River at Devalls Bluff, Arkansas and the 85 percentile of the national average concentrations. Number of fish in ().

	p'p' DDE	p'p'DDD	p'p'DDT	Dieldrin
Site 1				
Spotted Gar (1)	0.14	0.01	ND[1]	ND
Smallmouth Buffalo(3)	0.13	0.02	ND	0.01
Site 2				
White Crappie(1)	0.09	0.02	ND	0.02
Smallmouth Buffalo(3)	0.30	0.05	ND	0.03
Site 3				
Spotted Gar (1)	0.17	0.02	ND	0.01
Smallmouth Buffalo(2)	0.16	0.04	ND	0.04
Site 4				
Spotted Gar (1)	0.37	0.02	ND	0.01
Smallmouth Buffalo(2)	0.58	0.08	0.03	0.02
Site 5				
Spotted Gar (2)	0.20	0.02	ND	0.01
Smallmouth Buffalo(3)	0.64	0.10	0.05	0.04
Carp (1)	0.39	0.04	0.02	0.01
NCBP, White River, AR	0.13	0.03	0.03	0.06
Nat'l. 85%	0.22	0.07	0.04	0.04

1- Not detected

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Table 5. Weighted mean concentrations (ppm-wet weight) of organochlorines from fish samples collected in Cache River National Wildlife Refuge, May 1989. Range of values [ ]. See Table 3 for taxomonomic name and number of samples.

	DDE	DDD	DDT	Dieldrin
Spotted Gar	0.21 [0.14-0.37]	0.02 [ND-0.02]	ND ND	0.01 [ND-0.01]
White Crappie	0.09	0.02	ND	0.02
Smallmouth Buffalo	0.36 [0.13-0.64]	0.02 0.01-0.02]	0.02 [ND-0.05]	0.03 [0.01-0.04]
Carp	0.39	0.04	0.02	0.01

ND-Not Detected

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Table 6. Total concentrations (ppm, wet weight) of organochlorine compounds and aliphatic hydrocarbons from soil samples collected from near the air landing strip at Radcliffe Farms, Cache River National Wildlife Refuge, January 1991. See Figure 3 for location of sample sites.

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Organochlorine						
DDTM	ND	0.30	1.49	2.28	1.08	5.06
Toxaphene	ND	ND	3.8	7.6	0.62	.92
Aliphatic Hydrocarbons	2832.2	1564.1	1.76	3.73	3.47	0.51

Discussion

The priority pollutant inorganic compounds found on and near the CRR include chromium, copper, zinc, mercury, and selenium. Copper was highest in the fish tissue on the Cache River near the Highway 17 bridge crossing (Site 5). There are no predator protection levels for copper concentrations suggested in the literature. Further, there are no upper legal limits for copper in fish and fishery products in the United States; however, other countries have limits ranging from 10 to 100 ppm (Pastorok 1987). Possible sources of copper include soil erosion, urban runoff, corrosion of pipes, industrial discharges, and sewage treatment plant discharges (U.S. Environmental Protection Agency 1986).

Zinc concentrations in the CRR smallmouth buffalo tissue exceeded the 85 percentile at two of the sites (Site 2-Highway 33 and Site 5-Highway 17). Zinc may interact synergistically with copper and ammonia to produce an increased toxic effect on fish (Herbert and Vandyke 1964). There are no established limits for zinc in fish and fishery products in the United States. However, other countries have limits for zinc for fish and fishery resources ranging from 30 to 1,000 ppm (U.S. Environmental Protection Agency 1989). There is nothing in the literature to suggest a critical limit for the protection of fish and wildlife resources. Common sources of zinc are urban runoff, soil erosion, industrial discharges, and pesticides (U.S. Environmental Protection Agency 1980a).

Concentrations of mercury in the fish tissue from all the CRR sites were above the 85 percentile for national samples and above the NCBP White River samples. The mercury levels in the CRR fish ranged from 1.3 to 3.7 times higher than the 85 percentile found for the national survey. Mercury is one of few metals that: bioconcentrates and biomagnifies; has only harmful effects when present in fish and wildlife; is a carcinogen, mutagen, and teratogen; and is easily transformed from the less toxic inorganic form to a more toxic organic form in fish and wildlife tissues (Eisler 1987). Mercury predator protection levels for birds which consume fish and other organisms should not exceed 0.1 ppm (Eisler 1987). The U. S. Environmental Protection Agency (1980b) reported concentrations of mercury of 0.1 ppm fed to ducks reduced fertility and inhibited food conversion. In other countries, the legal limits for mercury in fish and fish products ranges from 0.1 to 1.0 ppm. The U.S. Food and Drug Administration does have an "action level" of 1.0 ppm. Some sources of mercury include sewage treatment plant discharges, paints, pesticide compounds, soil erosion, and air pollution deposition from fossil fuel combustion and smelters (Eisler 1987). Mercury can have a cumulative impact on a small river, due to it's persistence, and the fact that it does not breakdown easily. Consequently, mercury may accumulate in the sediments and biota (Irwin 1991).

Only the smallmouth buffalo from the Cache River near Highway 17 had concentrations of selenium in the tissue at levels that exceeded the levels found in the NCBP fish tissue from White River near Devalls Bluff, Arkansas. All levels of selenium in the fish tissue from the CRR were below the 85 percentile for the national survey.

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Non-priority inorganic compounds were also present in fish tissue samples, however, many of these compounds are not potentially harmful to fish and wildlife resources. Magnesium in the fish tissue ranged from around 1,300 parts per million (ppm) to over 10,000 ppm. The element occurs naturally in sediments, is one of the most common ions in freshwater, and is a major contributor to water hardness (U.S. Environmental Protection Agency 1986). Little is known concerning whether or not elevated levels of magnesium in animal tissues might be harmful to the organism or to fish and wildlife species which consume the organism (Irwin 1991).

Dieldrin was the only priority organic compound found in fish tissue samples. Dieldrin concentrations in the fish tissue from on and near the CRR were below the 0.1 ppm level set by the National Academy of Sciences (National Academy of Sciences, National Academy of Engineering 1973) for predator protection. All of the fish tissue samples also had total DDTM levels below the 1.0 ppm level established for predator protection (National Academy of Sciences, National Academy of Engineering 1973).

The soil samples collected from the Radcliffe Farm site had levels of DDT that exceeded the levels of DDD and even DDE, indicating either fairly recent usage of DDT or that the soils at this site do not allow for the DDT breakdown process to occur. The threshold levels of DDT in sediments were determined by Bolton et al. (1985) to be 0.006 ppm, dry weight. The determinations of organochlorine concentrations for the Radcliffe Farm site were all based on wet weight. Wet weight concentrations of a given sample will be less than dry weight concentrations due to the percent moisture of the sample and the total organic carbon content of the sample (which determines how much chemical can bind to the organic sediment particle). The level of DDTM established in 1990 by NOAA (Long and Morgan 1990) for coastal and estuarine environments for potential adverse biological effects was 7 parts per billion (ppb). With the exception of a sample collected near the fuel storage tanks, all of the soil samples collected on the Radcliffe Farm site have levels of DDT far above levels that are considered safe.

Soil samples at the Radcliffe Farm site also indicated very high levels of toxaphene. Toxaphene is an extremely persistent insecticide which is very toxic to non-target freshwater organisms and which can result in the death of these organisms at ambient water concentrations below 10 ppb (Eisler 1985). Stocks of toxaphene were allowed to be used through 1986. In soils, toxaphene can persist for lengthy periods (years) with microbial degradation occurring under aerobic and anaerobic conditions (Cohen et al. 1982). Toxaphene also bioaccumulates and biomagnifies through food chains (Eisler 1985). There is inadequate knowledge of the interactive effects of toxaphene with other agricultural chemicals such as DDT and its isomers and petroleum (Eisler 1985). The maximum allowable level of toxaphene in soils in the Soviet Union is 0.5 ppm (Beyer 1990). Threshold levels determined by Bolton et al. (1985) were 0.02 ppm, dry weight. The levels of toxaphene contamination in the soils from the Radcliffe Farm site are well above levels of toxaphene that are considered safe.

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Aliphatic hydrocarbons are a component of motor oil and other petroleum products. The levels of aliphatic hydrocarbons around the fuel storage tanks indicate that sloppy dispensing of fuel occurred over a period of time. Aliphatic hydrocarbons in soils are typically not biologically available. If aliphatics were present in sediment at high enough quantities to be biologically harmful, they would generally end up as tarballs and therefore not be biologically available (Clarke and Gibson 1987).

Recommendations

Additional studies should be conducted to determine possible source(s) of the inorganic and organic contaminants found on and near the CRR in order to control their release and control/reduce possible contamination of the Service's trust resources, particularly fish eating migratory birds. Levels of inorganic compounds detected in the fish tissue samples taken from on and near the CRR indicate that samples should be collected every few years to monitor levels of mercury and copper.

Sampling to determine the extent of DDTM and toxaphene contamination in the soils near the Radcliffe Farm landing strip site needs to be completed. These contaminated soils should be either removed for proper disposal or, depending on the leaching ability of the soils and the proximity of the ground water system, covered with at least 12 inches of clean top soil to make the soils unavailable to any fish and wildlife resources.

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Literature Cited

Beyer, W.N. 1990. Evaluating soil contamination. U.S. Fish and Wildl. Serv., Biological Rep. 90(2). 25 pp.

Bolton, S.H., R.J. Breteler, B.W. Vigon, J.A Scanlon, and S. L. Clark. 1985. National prospective on sediment quality. U.S. EPA, Office of Water Standards Div. Washington, D.C. 68 pp.

Clarke, J. U. and A.B. Gibson. 1987. Regulatory identification of petroleum hydrocarbons in dredged material; proceedings of a workshop. Misc. Paper D-87-3. U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi. 35 pp.

Cohen, D.B., G.W. Bowes, and S.M. Ali. 1982. Toxaphene. California State Water Res. Control Bd., Toxic Substances Control Prog., Spec. Proj. Rep., 82-4SP. 126 pp.

Eisler, R. 1985. Toxaphene hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildl. Serv. Biol. Rep. 85/1.4: 1-26.

____. 1987. Mercury hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildl. Serv. Biol. Rep. 85/1.10: 1-90.

Herbert, D.M. and J.M. Vandyke. 1964. The toxicity to fish of mixtures of poisons. Ann. Appl. Biol., 53: 415-421.

Irwin, R.J. 1991. Prototype Contaminants Encyclopedia. U.S. Fish and Wildl. Serv., Arlington, Texas. 1094 pp.

Long, E. and L.G. Morgan. 1990. The potential for biological effects of sediment-sorbed contaminants tested in the national status and trends program. NOAA Technical Memorandum NOS OMA 52, National Ocean Service, Seattle, Washington. 175 pp.

National Academy of Sciences, National Academy of Engineering. 1973. Water quality criteria 1972 (Blue Book). Ecological Research Series. EPA-R3-73-003. 594 pp.

Pastorok, P. 1987. Guidance manual for assessing human health risks from chemically contaminated fish and shell fish. PTI Environmental Service's submission to Battelle New England for EPA, Washington, D.C. PTI Environmental Draft Report C737-01. Bellevue, Washington. 91 pp.

Quackenbush, K.R., R.C. Barkley, and C.K. Baxter. 1984. Cache River Basin: a waterfowl habitat preservation proposal. Final Environmental Impact Statement. U.S. Fish and Wildl. Serv., Vicksburg, Mississippi. 115 pp.

Research Triangle Institute. 1990. Methodology: tissue sample preparation. Research Triangle Institute, Research Triangle Park, North Carolina. 2 pp.

Schmitt, C.J. and W. G. Brumbaugh. 1990. National contaminant biomonitoring program: concentration of arsenic, cadmium, copper, lead, mercury, selenium, and zinc in U.S. freshwater fish, 1976-1984. Arch. Environ. Contam. Toxicol. 19: 731-747.

State Chemical Laboratory. 1990. Method 1: analysis for organochlorine pesticides and PCBs in animal and plant tissue. Mississippi State University, Mississippi State, Mississippi. 3 pp.

_____. 1991. Method 4: analysis for organochlorine pesticides and PCBs, aliphatic and aromatic hydrocarbons in soil and sediment. Mississippi State University, Mississippi State, Mississippi. 1 pp.

U.S. Environmental Protection Agency. 1980a. Ambient water quality criteria for zinc. U.S. EPA Report 440/5-80-079. National Technical Information Service, Springfield, Virginia.

_____. 1980b. Ambient water quality criteria for mercury. U.S. EPA Report 440/5-80 -058. National Technical Information Service, Springfield, Virginia.

_____. 1986. Quality criteria for water. U.S. EPA Report 404/5-86-001, Office of Water Regul. and Stand. Washington, D.C. 237 pp.

_____. 1989. Assessing human health risks from chemically contaminated fish and shellfish: a guidance manual. EPA-503/8-89-002. Office of Water Regulations and Standards, Washington, D.C. 91 pp.

White, M. 1990. Return to the Cache. Arkansas Times, Little Rock, Arkansas. 7 pp.

APPENDIX A
Concentrations of Inorganic and Organic Compounds in Fish and Soil Samples for the Contaminants Survey of the Cache River National Wildlife Refuge

Table A1. Concentrations (mg/kg-ppm, dry weight) of inorganic compounds analyzed in fish samples collected from Site 1 (Grubbs, Arkansas) on the Cache River National Wildlife Refuge, May 1989.

	SG[1]-1	SMB[2]-1	SMB-1	SMB-1	Mean SMB-1
Aluminum (Al)	9	29	ND[3]	65	31.3
Barium (Ba)	25	22	24	20	22
Chromium (Cr)	5	3	2	2	2.3
Copper (Cu)	4	6	5	5	5.3
Iron (Fe)	97	200	183	165	182.7
Magnesium (Mg)	10161	1606	1651	1481	1579
Manganese (Mn)	96	44	40	37	40.3
Molybdenum (Mo)	7	5	4	3	4
Strontium (Sr)	137	66	61	55	60.7
Tin (Sn)	9	12	ND	3	5
Zinc (Zn)	86	62	69	60	63.7
Mercury (Hg)	1	1	1	1	1
Selenium (Se)	ND	1	ND	ND	ND

[1]SG-Spotted Gar
[2]SMB-Smallmouth Buffalo
[3]ND-Not Detected

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Table A2. Concentrations (mg/kg-ppm, dry weight) of inorganic compounds analyzed in fish samples from Site 2 (State Highway 33) on the Cache River National Wildlife Refuge, May 1989.

	WC[1]-2	SMB[2]-2	SMB-2	SMB-2	Mean SMB-2
Aluminum (Al)	11	39	13	102	51.3
Barium (Ba)	20	16	16	28	20
Chromium (Cr)	3	2	2	3	2.3
Copper (Cu)	4	7	5	6	6
Iron (Fe)	64	13	73	190	92
Magnesium (Mg)	1757	1356	1304	1857	1506.7
Manganese (Mn)	18	28	25	44	32.3
Molybdenum (Mo)	4	2	2	4	2.7
Strontium (Sr)	87	49	49	79	59
Tin (Sn)	18	8	5	16	9.7
Zinc (Zn)	78	57	49	70	58.7
Mercury (Hg)	1	1	1	1	1
Selenium(Se)	ND[3]	ND	ND	2	0.7

[1]WC-White Crappie
[2]SMB-Smallmouth Buffalo
[3]ND-Not Detected

Table A3. Concentrations (mg/kg-ppm, dry weight) of inorganic compounds analyzed in fish samples collected from Site 3 (Rex Hancock Wildlife Management Area) on the Cache River National Wildlife Refuge, May 1989.

	SG[1]-3	SMB[2]-3	SMB-3	Mean SMB-3
Aluminum (Al)	54	41	68	54.5
Barium (Ba)	20	20	23	21.5
Chromium (Cr)	5	3	2	2.5
Copper (Cu)	5	6	5	5.5
Iron (Fe)	137	111	124	117.5
Magnesium (Mg)	8799	1554	1520	1537
Manganese (Mn)	117	47	52	49.5
Molybdenum (Mo)	6	3	4	3.5
Strontium (Sr)	84	64	58	61
Tin (Sn)	15	22	20	21
Zinc (Zn)	65	60	1429	744.5
Mercury (Hg)	2	1	1	1
Selenium(Se)	ND[3]	ND	ND	ND

[1]SG-Spotted Gar
[2]SMB-Smallnouth Buffalo
[3]ND-Not Detected

Table A4. Concentrations (mg/kg-ppm, dry weight) of inorganic compounds analyzed in fish samples collected from Site 4 (mouth of Cache Bayou) on Cache River National wildlife Refuge, May 1989.

	SG[1]-4	SMB[2]-4	SMB-4	Mean SMB-4
Aluminum (Al)	56	265	285	275
Barium (Ba)	26	23	27	25
Chromium (Cr)	6	3	3	3
Copper (Cu)	4	5	7	6
Iron (Fe)	176	342	523	432.5
Magnesium (Mg)	9776	1625	1642	1633.5
Manganese (Mn)	167	68	110	89
Molybdenum (Mo)	7	4	3	3.5
Strontium (Sr)	111	44	49	46.5
Tin (Sn)	20	4	21	12.5
Zinc (Zn)	88	57	63	60
Mercury (Hg)	1	1	2	1.5
Selenium (Se)	ND[3]	1	ND	0.5

[1]SG-Spotted Gar
[2]SMB-Smallmouth Buffalo
[3]ND-Not Detected

Table A5. Concentrations (mg/kg-ppm, dry weight) of inorganic compounds analyzed in fish samples collected from Site 5 (Highway 17) on the Cache River National Wildlife Refuge, May 1989.

	SG[1]-5	SG-5	Mean SG-5	SMB[2]-5	SMB-5	SMB-5	Mean SMB-5	CP[3]-5
Aluminum (Al)	10	13	11	55	74	68	66	53
Barium (Ba)	29	36	32	20	19	19	19	21
Chromium (Cr)	5	6	6	3	2	2	2	2
Copper (Cu)	24	4	14	7	8	10	8	9
Iron (Fe)	104	102	103	138	183	141	154	159
Magnesium (Mg)	8789	10819	9804	1607	1327	1432	1455	1372
Manganese (Mn)	146	118	132	45	35	32	37	18
Molyb denum(Mo)	4	6	5	4	4	4	4	2
Strontium (Sr)	143	188	166	63	46	47	52	49
Tin (Sn)	20	24	22	20	9	19	16	24
Zinc (Zn)	74	89	44	61	46	55	54	287
Mercury (Hg)	2	1	1.5	2	2	1	1.7	1
Selenium (Se)	1	ND[4]	0.5	ND	2	1	1	2

[1]SG-Spotted Gar
[2]SMB-Smallmouth Buffalo
[3]CP-Carp
[4]ND-Not Detected

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Table A6. Concentrations (ppm-wet weight) of organochlorine compounds analyzed, total weight, percent moisture, and percent lipid in fish collections from the Cache River National Woldlife Refuge, May 1989. Other OC's analyzed but all below detection limits.

	p'p' DDE	p'p'DDD	p'p'DDT	Dieldrin		Wt.	% mois	% Lip
Site 1								
Spotted Gar	0.14	0.01	ND[1]	ND		1230	74	1.14
S.mouth Buffalo	0.14	0.02	ND	0.01		4480	71	5.7
S.mouth Buffalo	0.12	0.03	ND	0.01		2450	74	5.48
S.mouth Buffalo	0.14	0.02	ND	0.02		3100	73.2	5.56
Mean SMBU	0.13	0.02	ND	0.01		3343	72.7	5.58
Site 2								
W. Crappie	0.09	0.02	ND	0.02		649	74.2	2.54
S.mouth Buffalo	0.29	0.05	ND	0.04		5430	79.4	7.78
S.mouth Buffalo	0.39	0.07	ND	0.04		5350	77.4	9.78
S.mouth Buffalo	0.21	0.03	ND	0.02		5250	80.0	5.10
Mean SMBU	0.30	.05	ND	0.03		5381	78.9	7.55
Site 3								
Spotted Gar	0.17	0.02	ND	0.01		894	70.8	2.4
S.mouth Buffalo	0.15	0.05	ND	0.04		4080	76.6	11.1
S.mouth Buffalo	0.16	0.04	ND	0.03		3880	79.2	9.80
Mean SMBU	0.16	0.04	ND	0.04		3980	77.9	10.4

Table A6 Continued

	p'p'DDE	p'p'DDD	p'p'DDT	Dieldrin		Wt	% Mois	% Lip
Site 4								
Spotted Gar	0..37	0.02	ND	0.01		1070	69.5	6.58
S. mouth Buffalo	0.58	0.07	0.03	0.03		4000 .	70.5	8.04
S.mouth Buffalo	0.59	0.08	0.03	0.02		3040	72	6.66
Mean SMBU	0.58	0.08	0.03	0.02		3520	71.2	7.4
Site 5								
Spotted Gar	0.23	0.03	ND	0.01		1810	68	2.46
Spotted Gar	0.16	0.01	ND	0.01		1440	71.5	2.16
Mean Gar	0.20	0.02	ND	0.01		1625	69.8	2.31
S.mouth Buffalo	0.40	0.06	0.03	0.04		6420	69.5	8.16
S.mouth Buffalo[1]	0.93	0.13	0.06	0.05		5790	70.5	9.84
S.mouth Buffalo[1]	0.58	0.10	0.05	0.03		5770	71.5	9.02
Mean SMBU	0.64	0.10	0.05	0.04		5993	70.5	9.0

[1]ND-Not Detected

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Table A7. Concentrations (mg/kg-ppm, wet weight) of organochlorine compounds detected in sediment samples collected near the air landing strip on Radcliffe Farms, Cache River National Wildlife Refuge, January 1991.

ORGANOCHLORINE PESTICIDES	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
beta - BHC (c)[1]	ND[3]	ND	.02	.02	.02	.06
alpha chlordane (c)	ND	ND	.01	ND	ND	ND
trans-nanochlor	ND	ND	.02	.03	ND	.01
Toxaphene (c)	ND	ND	3.8	7.6	.62	.92
o'p'-DDE	ND	ND	ND	.02	.01	.03
o'p'-DDD	ND	ND	.05	.14	.06	.62
o'p'-DDT	ND	ND	.19	.29	.10	.21
p'p'-DDE (c)	ND	.09	.58	.48	.43	1.4
p'p'-DDD (c)	ND	ND	.19	.37	.13	1.6
p'p'-DDT (c)	ND	.21	.48	.98	.35	1.2
Dieldrin (c)	ND	ND	.01	ND	.02	.04
Endrin	ND	ND	.01	ND	ND	ND
TOTAL DDTM[2]	ND	.30	1.49	2.28	1.08	5.06
Detection limits sediments/soils 0.01 ppm OC's 0.05 ppm Tox/PCB						

[1]carcinogenic
[2]DDT and metabolites
[3]ND-Not Detected

Table A8. Concentrations (mg/kg-ppm) of aliphatic hydrocarbons in sediments collected from near the air strip on Radcliffe Farms, Cache River National Wildlife Refuge, January 1991. Lower Level of Detection = 0.01 ppm.

ALIPHATIC HYDROCARBONS (AHS)	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
n-dodecane (n-c12)	2.3	.22	.01	.01	.01	.03
n-tridecane (n-c13)	9.4	2.1	.01	.01	.02	.02
n-tetradecane (n-c14)	40.0	19.0	.02	.01	.02	.01
n-pentadecane (n-c15)	130.0	72.0	.05	.04	.04	.01
n-hexadecane (n-c16)	250.0	140.0	.08	.10	.10	.02
n-heptadecane (n-c17)	360.0	190.0	.13	.23	.21	.04
n-octadecane (n-c18)	370.0	180.0	.16	.33	.30	.05
n-nonodecane (n-c19)	290.0	130.0	.14	.27	.23	.06
n-eicosane (n-c20)	240.0	120.0	.20	.29	.20	.08
octylcyclohexane	9.5	6.9	ND[1]	ND	ND	ND
nonylcyclohexane	82.0	64.0	.03	.04	.04	ND
pristane	570.0	370.0	.39	1.2	1.2	.09
phytane	470.0	270.0	.54	1.2	1.1	.10
TOTAL ALIPHATIC HYDROCARBONS	2832.2	1564.1	1.76	3.73	3.47	.51

[1]ND-Not Detected

1989 - initial survey / fish samples
fish
99 - soil samples = not Hg?

all sites for
- fish exceed 85%ile for Hg national samples and > NCBP White River samples
[range = 1.3 - 3.7 x higher]

Hg predator protection level (for fish. birds) shouldn't exceed @ 0.1 ppm (wet wt)

Recs

additional study extent of contam source

Continue monitoring of bird/Hg levels in fish

UAFT - NCBP - collected @ White River near DeValls Bluff Arkansas (Schmitt + Brumbaugh, 1990)
85%ile of mean values from all US samples
>85%ile = elevated

Matrix	Contaminant	Concentration Mean (min-max)	Site	Date	Water, Soil or Sediment Criteria	RPT 5	
						cache	
Species	**Contaminant**	**Concentration Mean (min-max) ppm ww**	**Tissue**	**Date**	**Threshold Concentration**		
spotted gar	mercury	0.30		1989	0.18 = 85%ile of nat.		
		0.66			avg. concentrations		
		0.46					
		0.41					
smallmouth buffalo		0.26					
		0.30					
		0.24					
		0.44					
		0.43					
white crappie		0.34					
carp		0.36					
Species	**Endpoint**	**Effect**					